

The Yield of CO from the Reaction of CH₃ and O Atoms

Jack M. Preses, Christopher Fockenberg and James T. Muckerman
Chemistry Department
Brookhaven National Laboratory
Upton, NY 11973-5000

In the combustion of methane under lean-to-moderately rich conditions, the reaction of methyl radicals and ground-state oxygen atoms plays a pivotal role.¹ The branching ratios among the various products have been the subjects of considerable study, as cited in Ref. 1. Possible channels include:



Reports of the relative importance of reactions 1a-e vary, and in Ref. 1 we attempt to determine the relative yields of these reactions at room temperature using our time-of-flight (TOF)-based combustion kinetics apparatus. The yield of CO from reactions (1) is the subject of some controversy. Slagle *et al.*³ report that channel (1a) is the only important one between 294 and 900 K, while Seakins and Leone⁴ measure an overall yield of CO of 0.4 ± 0.2 . Our time-of-flight measurements indicated a CO yield of 0.17 ± 0.11 . To obtain a definitive branching fraction for the production of CO, we decided to determine the CO yield using a direct, unambiguous spectroscopic method, tunable diode laser spectroscopy.

The concept of our experiment is simple: fill a static cell with stable precursors to CH₃ radicals and O atoms and a buffer gas. Irradiate the cell with 193-nm excimer laser radiation to photolyze the precursors. The CH₃ radicals and O atoms will then react forming, among other products, CO. A diode laser tuned to a CO absorption probes the reaction mixture after complete equilibration and the CO concentration is determined from the magnitude of the absorption. Comparison of the CO concentration with other species concentrations (e.g. formaldehyde increase, methyl precursor decrease) ought to produce the CO branching ratio. In practice, however, a number of complications must be overcome to produce a valid determination.

First, there are (at least) two sources of CO in the experiment. The photochemical precursor to CH₃ radicals is acetone, CH₃COCH₃. The 193-nm photolysis of this molecule produces not only two CH₃ radicals, but a CO molecule that must be distinguished from the CO product of radical-radical reactions. Second, radical concentrations must be adjusted so that radical-radical reactions competing with CH₃ + O do not distort the result. The solution for the first problem is to use isotopically labeled acetone. Acetone 99% labeled with ¹³C on the methyls and ¹²C on the carbonyl is commercially available. Therefore, in the absence of other reactions that make ¹³CO, ¹²CO is produced from the direct photolysis and ¹³CO is produced from reactions of CH₃. The branching fraction is then simply given by $\frac{1}{2} \times [\text{13CO}] / [\text{12CO}]$.

There are at least two regions of the CO spectrum accessible to our laser diode where easily identified ^{12}CO and ^{13}CO ground-state rovibrational lines lie within 0.3 cm^{-1} of one another. We adjust precursor pressures to reduce competition from other radical-radical reactions. We also demonstrate that under the conditions of our experiment, ^{13}CO produced from 193-nm photolysis of formaldehyde produced by reaction (1a) does not significantly distort our results.

A summary of the data is shown in Fig. 1. The branching ratio for CO production extrapolated to zero products is $0.18 \pm .04$ in excellent agreement with that measured in the TOF study, with considerably smaller error limits.

The TOF study of the reaction of CH_3 and O is being extended to higher temperatures. As with those experiments. These measurements are also being performed as a function of temperature. These temperature range of these experiments will ultimately be limited by linewidth considerations

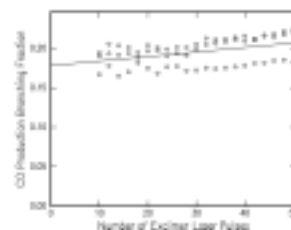


Figure 1. The branching ratio for the production of CO from reactions (1). Three experimental runs with total pressure 5 Torr, $[\text{SO}_2] = 50\text{ mTorr}$ $[\text{Acetone}] = 4\text{ mTorr}$

Acknowledgment

This work was performed at Brookhaven National Laboratory under Contract DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

References

- 1 C. Fockenberg, G. E. Hall, J. M. Preses, T. J. Sears, and J. T. Muckerman, *J. Phys. Chem. A* **103**, 5722-5731 (1999).
- 2 C. Fockenberg, H. J. Bernstein, G. E. Hall, J. T. Muckerman, J. M. Preses, T. J. Sears, and J. Ralph E. Weston, *Rev. Sci. Instrum* **70**, 3259-3264 (1999).
- 3 I. R. Slagle, D. Sarzynski, and D. Gutman, *J. Chem. Soc., Faraday Trans.* **84**, 491-503 (1988).
- 4 P. W. Seakins and S. R. Leone, *J. Phys. Chem* **96**, 4478 (1992).